Arabian Journal of Chemistry (2016) 9, S1410–S1415

King Saud University

Arabian Journal of Chemistry

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REVIEW

FTIR study of hydrogen bonding between substituted benzyl alcohols and acrylic esters

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Received 22 November 2011; accepted 14 March 2012
Available online 28 March 2012

KEYWORDS

Benzyl alcohol;
Acrylic esters;
Formation constant;
Hydrogen bonding

Abstract Hydrogen bonding between substituted benzyl alcohols (benzyl alcohol, *o*-aminobenzyl alcohol, *o*-chlorobenzyl alcohol and *o*-nitrobenzyl alcohol) and acrylic esters (methyl methacrylate, ethyl methacrylate) is studied in carbon tetrachloride by using the FTIR spectroscopic method. Utilizing the Nash method, the formation constant (K) of the 1:1 complexes is calculated. Using the K value, the Gibbs free energy change (ΔG^0) is also calculated. The calculated formation constant and Gibbs free energy change values vary with the substituent of benzyl alcohol and ester chain length, which suggests that the proton donating ability of substituted benzyl alcohols is in the order: *o*-aminobenzyl alcohol < benzyl alcohol < *o*-chlorobenzyl alcohol < *o*-nitrobenzyl alcohol, and proton accepting ability of acrylic esters is in the order: methyl methacrylate < ethyl methacrylate.

Contents

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2012.03.007

1. Introduction

Benzyl alcohol is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings. It is also a precursor to a variety of esters, used in the soap, perfume, and flavor industries, as well as for pharmaceuticals (Huang et al., 2008). It exhibits bacteriostatic and antipruritic properties. It is also used as a photographic developer. Acrylic esters are industrially important chemicals and precursors in the synthesis of polymers (Schildknecht, 1977). Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. The study of the H-bonds of the type O–H···O═C occupies a position of considerable importance as it relates to the study of biopolymers. Thus the study and knowledge of properties of the ternary mixtures of acrylic esters with aromatic alcohols in non-polar solvents are expected to provide useful and vital process parameters for the efficient design of transesterification processes of industrial interest. Studies of the interaction between associated and non-associated liquids in inert media provide valuable information regarding molecular complex formation in solution. Infrared studies of methyl methacrylate and ethyl methacrylate in various solvents have been reported by Liu et al. (2004) and Zheng et al. (2004). Rosenberg and Smith (1963) calculated the equilibrium constant of aliphatic esters-alcohol systems. Krueger and Hawkins (1973) reported the OH stretching frequency of substituted benzyl alcohols (methoxy, methyl, chloro and nitro) in carbon tetrachloride using infrared technique. Dharmalingam et al. (2006a,b) have reported the hydrogen bonding between acrylic esters with aliphatic alcohols in non-polar solvents through FTIR study. FTIR investigation of the properties of organic compounds is of great value in understanding the nature of molecular interaction between the molecules. Keeping both the industrial and scientific interests in mind, we report here the results of our investigation on the H-bonded complexes of substituted benzyl alcohols with acrylic esters in carbon tetrachloride using FTIR spectroscopic measurement. This study is expected to provide better understanding of the nature of molecular orientation processes and also the main objectives of this study are twofold: (1) to see the role of substituent change in benzyl alcohol on the strength of the hydrogen bonding between free hydroxyl group of alcohol and carbonyl group of ester and (2) to elucidate the effect of the medium, and particularly the role of specific solute–solute interactions on the stability of 1:1 complex formation between substituted benzyl alcohol and acrylic ester.

2. Experimental section and method

2.1. Materials

Methyl methacrylate, ethyl methacrylate, benzyl alcohol, *o*-aminobenzyl alcohol, *o*-chlorobenzyl alcohol and *o*-nitrobenzyl alcohol with purity >99% (spectroscopic grade) were purchased from Aldrich and used without any further purification. AR grade carbon tetrachloride was purified by standard method (Weissberger, 1970) and redistilled before use. The physical parameters of all the chemicals used in this study were checked against their literature values.

2.2. FTIR measurements

A Nicolet Avatar 360 FTIR spectrometer with a resolution of $\pm 1\ cm^{-1}$ was used. Spectra were recorded at 298 K in the region of 4000–400 cm^{-1}, and NaCl cell of path length 0.1 mm was used. The spectrometer possesses auto align energy optimization and dynamically aligned interferometer. It is fitted with a KBr beam splitter, a DTGS-Detector and Everlgo™ mid-IR source. A baseline correction was made for the spectra recorded.

3. Results and discussion

The observed spectral data of primary alcohols (*o*-aminobenzyl alcohol, benzyl alcohol, *o*-chlorobenzyl alcohol and *o*-nitrobenzyl alcohol) with carbon tetrachloride are reported in Table 1. Benzyl alcohols in carbon tetrachloride exhibit two hydroxyl bands in the region from 3700 to 3300 cm^{-1}, i.e., one is due to monomeric (O–H free) and the other is due to polymeric absorption (O–H bonded) (Kirsch and Coffin, 1976). The frequency difference between the free monomeric O–H (ν_{free}) and bonded O–H bands (ν_{bond}) is $\Delta\nu_{OH}$ (i.e., $\Delta\nu = \nu_{free} - \nu_{bonded}$) is shown in Table 1. It is observed that, free hydroxyl band, bonded hydroxyl band and $\Delta\nu_{OH}$ values vary with the substituent of benzyl alcohol. The infrared spectral parameter ν_{OH} free increases in the order: *o*-aminobenzyl alcohol < benzyl alcohol < *o*-chlorobenzyl alcohol < *o*-nitrobenzyl alcohol. But, no linear variations with substitution of benzyl alcohols are observed for bonded hydroxyl bond and $\Delta\nu_{OH}$ values. Similar results were observed for benzyl alcohol in carbon tetrachloride by Forland et al. (1997), Bellamy and Pace (1971) and Richards (1948). The spectral data of the acrylic esters (methyl methacrylate (MMA), and ethyl methacrylate (EMA)) in carbon tetrachloride are given in Table 2. From Table 2, the carbonyl absorption band of the acrylic esters in carbon tetrachloride is observed in the order: methyl methacrylate > ethyl methacrylate. Similar result is observed by Nyquist and Streck (1994) in acrylic esters with carbon tetrachloride.

For ternary mixtures, the proton acceptor (acrylic esters) concentration is fixed at 0.03 $mol\,l^{-1}$, varying the proton

Table 1 Spectral data for substituted benzyl alcohols in carbon tetrachloride at 298 K.

Proton donor	ν_{OH} free (cm^{-1})	ν_{OH} bonded (cm^{-1})	$\Delta\nu_{OH}$ (cm^{-1})
o-Aminobenzyl alcohol	3612	3386	226
Benzyl alcohol	3617	3489	128
o-Chlorobenzyl alcohol	3619	3488	131
o-Nitrobenzyl alcohol	3622	3348	274

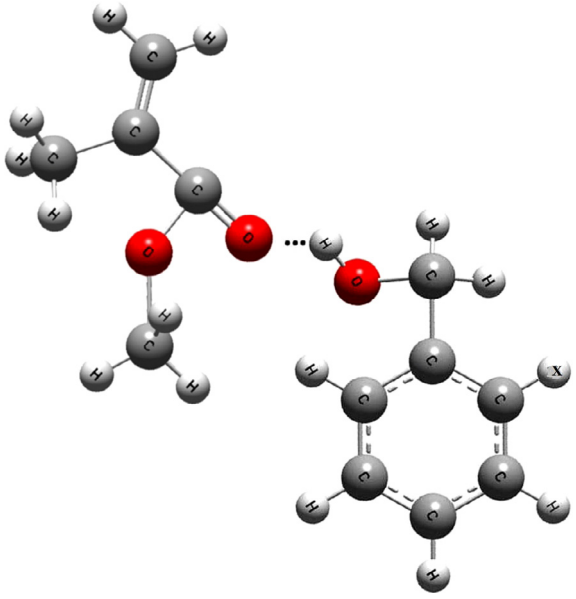

Figure 1 Hydrogen bonding between substituted benzyl alcohols and methyl methacrylate X = NH_2 (*o*-aminobenzyl alcohol), H (benzyl alcohol), Cl (*o*-chlorobenzyl alcohol), NO_2 (*o*-nitrobenzyl alcohol).

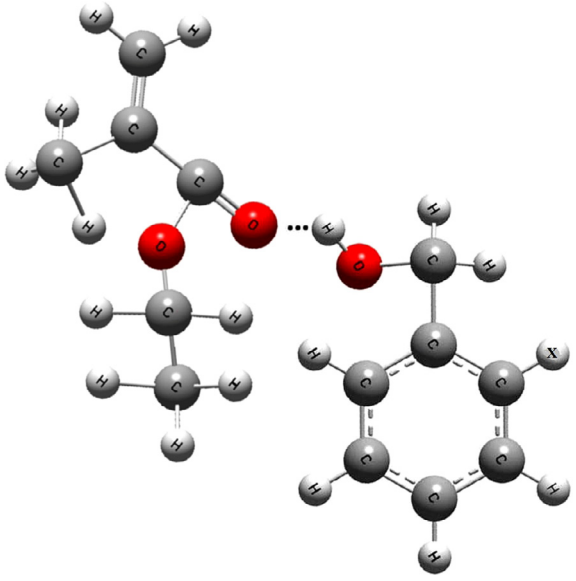

Figure 2 Hydrogen bonding between substituted benzyl alcohols and ethyl methacrylate X = NH_2 (*o*-aminobenzyl alcohol), H (benzyl alcohol), Cl (*o*-chlorobenzyl alcohol), NO_2 (*o*-nitrobenzyl alcohol).

donor (substituted benzyl alcohols) concentrations from 0.03 to 0.15 mol l^{-1}. By changing the concentrations, the free O–H band intensity and half-bandwidth increases with increasing benzyl alcohol concentrations. But, at the same time the reverse trend is noticed for the carbonyl absorption band. The absorbance values of O–H and C=O are given in Tables 3 and 4. From the observation, it indicates that the existence of 1:1 complex formation between the free hydroxyl group of

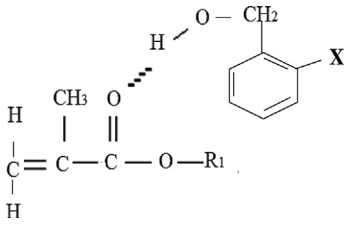

Figure 3 Hydrogen bonding between substituted benzyl alcohols and acrylic esters R_1 = CH_3 (methyl methacrylate), C_2H_5 (ethyl methacrylate) X = NH_2 (*o*-aminobenzyl alcohol), H (benzyl alcohol), Cl (*o*-chlorobenzyl alcohol), NO_2 (*o*-nitrobenzyl alcohol).

substituted benzyl alcohols and the carbonyl group of acrylic esters (MMA and EMA) (i.e., O–H···O=C) (Figs. 1 and 2). Simple structure diagram of 1:1 complex formation between substituted benzyl alcohols and acrylic esters (MMA and EMA) is shown in Figs. 3. This type of 1:1 complex formation between methacrylates and phenol in carbon tetrachloride system was reported by Khan and Sivagurunathan (2008).

The association between an aromatic alcohol molecule (donor A), an acrylic ester (acceptor B) and complex AB can be represented by the equilibrium $A + B \leftrightarrow AB$, if only 1:1 complexes are present. The formation constant (K) for the 1:1 complex is calculated with the help of Nash (1960) method. In this method, at low concentration of alcohol, the influence of the higher order complexes on the absorption spectrum of the base is neglected. The concentrations of the proton donor [A], proton acceptor [B] and complexed species [AB] involved in the interaction are assumed to be obeying Beer's law at a given characteristic frequency of the 1:1 complex. The total absorbance per centimeter path of B is given by

$$A = \varepsilon_b[B] + \varepsilon_{ab}[AB] \tag{1}$$

where ε_b and ε_{ab} are the molar absorptivities of the species B and complexed species AB, respectively. In the absence of a complexing agent 'A' the total absorbance per centimeter is given by

$$a_0 = \varepsilon_b[B^0] \tag{2}$$

where $[B^0]$ is the initial concentration of B.

Dividing Eq. (1) by (2)

$$\frac{a}{a_0} = \frac{[B]}{[B^0]} + \frac{[AB]}{[B^0]} \cdot \frac{\varepsilon_{ab}}{\varepsilon_b} \tag{3}$$

The formation constant K may be defined as

$$K = \frac{[AB]}{[A][B]} \tag{4}$$

Combining Eqs. (3) and (4)

$$\frac{a}{a_0} = \frac{[B]}{[B^0]}\left[1 + \frac{\varepsilon_{ab}}{\varepsilon_b}[A]\right] \tag{5}$$

Table 2 Spectral data for methyl methacrylate and ethyl methacrylate in carbon tetrachloride at 298 K.

Proton acceptor	$\nu_{C=O}$ (cm^{-1})
Methyl methacrylate	1726
Ethyl methacrylate	1720

Table 3 Absorbance of O–H and C=O bands at various concentrations of substituted benzyl alcohols with methyl methacrylate in carbon tetrachloride.

Concentration (mol/l)	Absorbance							
	o-Aminobenzyl alcohol		Benzyl alcohol		*o*-Chlorobenzyl alcohol		*o*-Nitrobenzyl alcohol	
	(O–H)	(C=O)	(O–H)	(C=O)	(O–H)	(C=O)	(O–H)	(C=O)
0.03	0.0631	0.8963	0.0827	0.8841	0.0839	0.8798	0.1114	0.8643
0.05	0.0892	0.8892	0.1167	0.8763	0.1207	0.8704	0.1532	0.8542
0.07	0.0985	0.8823	0.1396	0.8702	0.1482	0.8596	0.2087	0.8462
0.09	0.1248	0.8772	0.1591	0.8624	0.1713	0.8561	0.2386	0.8424
0.11	0.1597	0.8706	0.1943	0.8535	0.2186	0.8422	0.2614	0.8306
0.13	0.1786	0.8624	0.2085	0.8462	0.2407	0.8354	0.3371	0.8195
0.15	0.2304	0.8563	0.2802	0.836	0.3132	0.8251	0.3765	0.8112

Table 4 Absorbance of O–H and C=O bands at various concentrations of substituted benzyl alcohols with ethyl methacrylate in carbon tetrachloride.

Concentration (mol/l)	Absorbance							
	o-Aminobenzyl alcohol		Benzyl alcohol		*o*-Chlorobenzyl alcohol		*o*-Nitrobenzyl alcohol	
	(O–H)	(C=O)	(O–H)	(C=O)	(O–H)	(C=O)	(O–H)	(C=O)
0.03	0.0724	0.9084	0.0926	0.8966	0.0993	0.8848	0.1328	0.8698
0.05	0.0905	0.9016	0.1249	0.8898	0.1375	0.8751	0.1823	0.8611
0.07	0.1274	0.8943	0.1678	0.8832	0.1775	0.8701	0.2245	0.8503
0.09	0.1643	0.8904	0.1974	0.8776	0.2088	0.8673	0.2579	0.8491
0.11	0.1972	0.8861	0.2261	0.8693	0.2418	0.8572	0.3007	0.8392
0.13	0.2375	0.8795	0.2686	0.8633	0.2921	0.8427	0.3916	0.8307
0.15	0.2762	0.8763	0.3116	0.8539	0.3375	0.8298	0.4425	0.8191

Table 5 Formation constant (K) and free energy change (ΔG^0) for substituted benzyl alcohols with methyl methacrylate and ethyl methacrylate in carbon tetrachloride at 298 K.

Proton donor	Proton acceptor			
	Methyl methacrylate		Ethyl methacrylate	
	K (l mol^{-1})	ΔG^0 (kcal mol^{-1})	K (l mol^{-1})	ΔG^0 (kcal mol^{-1})
o-Aminobenzyl alcohol	5.19	0.97	5.61	1.02
Benzyl alcohol	6.58	1.12	7.45	1.19
o-Chlorobenzyl alcohol	8.28	1.25	9.57	1.34
o-Nitrobenzyl alcohol	11.64	1.45	13.10	1.52

Introducing the conservation of species of B

$$[B^0] = [B] + [AB] \tag{6}$$

Invoking Eq. (4) one can find that

$$\frac{[B]}{[B^0]} = (1 + K[A])^{-1} \tag{7}$$

when Eq. (7) is substituted in Eq. (5)

$$\frac{a}{a_0} = \frac{1 + \frac{\varepsilon_{ab}}{\varepsilon_b} K[A]}{1 + K[A]} \tag{8}$$

Taking

$$\frac{a}{a_0} = Z \tag{9}$$

$$K\frac{\varepsilon_{ab}}{\varepsilon_b} = \alpha \tag{10}$$

and $[A] = \frac{1}{Y}$Eq. (8) becomes

$$Z = \frac{1 + \frac{\alpha}{Y}}{1 + \frac{K}{Y}} \tag{11}$$

$$Y = \frac{ZK - \alpha}{1 - Z} \tag{12}$$

Expressing

$$X = \frac{1}{1 - Z}$$

$$X = \frac{1}{1 - \frac{a}{a_0}}$$

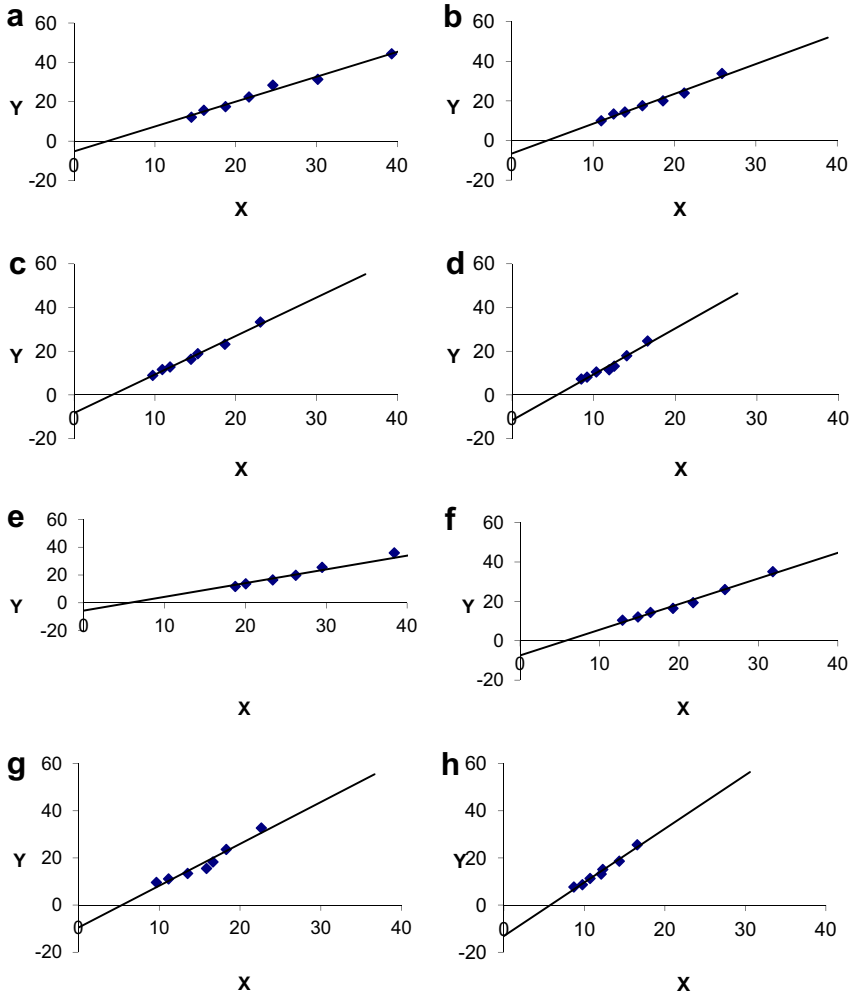

Figure 4 Formation constant for the 1:1 complex of substituted benzyl alcohols with acrylic esters (MMA and EMA). Methyl methacrylate with (a) *o*-aminobenzyl alcohol, (b) benzyl alcohol, (c) *o*-chlorobenzyl alcohol and (d) *o*-nitrobenzyl alcohol. Ethyl methacrylate with (e) *o*-aminobenzyl alcohol, (f) benzyl alcohol, (g) *o*-chlorobenzyl alcohol and (h) *o*-nitrobenzyl alcohol.

Since $Z = \frac{a}{a_0}$where a and a_0 are the absorbance of the carbonyl band of acrylic ester in the presence and absence of substituted benzyl alcohol, respectively.Eq. (12) rewrite in the form of linear equation as

$$Y = X(K - \alpha) - K \tag{13}$$

The physical significance of Eq. (13) is quite clear. When the reciprocal of the donor concentration ($Y = [A]^{-1}$) is plotted against the reciprocal of one minus absorbance ratio ($X = 1/$) ($1-(a/a_0)$) gives a straight line for 1:1 complex formation. The intercept of the plot of Y against X gives the negative value of the formation constant K. This type of plot is shown in Fig. 4. The Gibb's free energy change (ΔG^0) of the systems was calculated using the following relation (Vinogradov, 1971):

$$\Delta G^0 = -RT \ln K$$

where R, T and K represent the universal gas constant, absolute temperature, and formation constant of the relative systems, respectively.

The value of the formation constants and the Gibb's free energy changes for all the systems are provided in Table 5. It has been found that two opposing effects are possibly operative in these mixtures; namely, specific interactions between the carbonyl group of the ester and the free O–H group of the alcohol, and non-specific interactions (i.e., the breaking of intermolecular hydrogen bonds in the substituted benzyl alcohol).

The formation constant (K) and free energy change (ΔG^0) values for substituted benzyl alcohols with acrylic esters (MMA, EMA) in carbon tetrachloride solution are increasing in the order: *o*-aminobenzyl alcohol < benzyl alcohol < *o*-chlorobenzyl alcohol < *o*-nitrobenzyl alcohol. This change in K and ΔG^0 values indicates that the proton donating ability of the proton donor varies with the substituted benzyl alcohols. The infrared spectral parameters ν_{OH} free increase with substituent of benzyl alcohols in the binary system are linearly correlated with the proton donating ability of alcohols which gets reflected by the higher values of K and ΔG^0. The calculated K and ΔG^0 values for *o*-aminobenzyl alcohol with all of the proton acceptors are found to be smaller than those of benzyl alcohol, *o*-chlorobenzyl alcohol and *o*-nitrobenzyl alcohol with the same acceptors (EMA or MMA), which reveals that the proton donating ability of *o*-aminobenzyl alcohol is less

than that of benzyl alcohol, *o*-chlorobenzyl alcohol and *o*-nitrobenzyl alcohol. This may be due to the reason that the proton donating ability is positively correlated to the acidity of substituted benzyl alcohols which are increasing in the same sequence. By changing the type and number of substituents in benzyl ring the acidity can be regulated almost continuously. In addition, the formation constant (K) and free energy change (ΔG^0) value decrease for the electron donating group (i.e., amino) and increase for the electron withdrawing groups (i.e., chloro and nitro) when compared with benzyl alcohol. This is because the electron donating substituents facilitate the bond breaking process, whereas the electron withdrawing groups facilitate the bond making process. This is well reflected with a lower formation constant and free energy change values for electron donating groups and higher formation constant and free energy change values for electron withdrawing groups with the same acceptor (MMA or EMA). Our result that is in close agreement with the formation constant value was reported by Vanderheyden and Zeegers-Huyskens (1983) in phenol derivatives with acrylic esters.

The K and ΔG^0 values for substituted benzyl alcohols + methyl methacrylate system are found to be smaller than those of the substituted benzyl alcohols + ethyl methacrylate system. This may be attributed to the difference in basicity of the alkyl groups that varies in the order: methyl < ethyl (Singh and Saxena, 1983). This is because the negative inductive effect of the alkyl groups increases in the order methyl to ethyl, and the electron contribution of the ethyl group to the C═O group is significantly greater than that from the methyl group. Therefore, one would expect that the strongest intermolecular hydrogen bonds formed would be between the C═O group of ethyl methacrylate and the O–H proton of *o*-nitrobenzyl alcohol, with the weakest intermolecular hydrogen bonds between the C═O group of methyl methacrylate and the O–H proton of *o*-aminobenzyl alcohol.

4. Conclusion

From this study, it may be concluded that the proton donating ability of substituted benzyl alcohols and the proton accepting ability of acrylic esters vary linearly with the substitution in benzyl alcohols and the carbon chain length of acrylic esters.

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